

Sulfur- and Water-Tolerance of Pt/KL Aromatization Catalysts Promoted with Ce and Sulfur- and Water-Tolerance of Pt/KL Aromatization Catalysts Promoted with Ce and Yb

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Beamline(s): X18B

Introduction: The exceptionally high activity and selectivity of Pt/KL catalysts for n-hexane aromatization have been known for two decades and form the basis of a commercial process. A shortcoming of these catalysts is their extremely high sensitivity to even traces of sulfur (e. g. , parts per billion) . Acceptable aromatization performances can only be achieved by reducing the sulfur concentration in the feed to extremely low levels, which significantly raises the cost of the process. Therefore, the development of Pt/KL catalysts able to withstand higher sulfur concentrations than those used today appears as an attractive goal. In previous work, sulfur poisoned Pt/KL catalysts have been characterized by TEM , EXAFS , and DRIFTS of adsorbed CO. Those studies demonstrated that Pt particle growth is accelerated in the presence of sulfur, leading to zeolite pore plugging and significant losses in catalytic activity. All catalysts tested on the present work were characterized before and after reaction by a number of techniques. In agreement with previous studies, FTIR of adsorbed CO and chemisorptions results indicated that the Vapor Impregnation method resulted in higher Pt dispersion than that obtained by the IWI method. After reaction in the presence of sulfur, the Ce-promoted Pt/KL catalyst showed a higher resistance to metal agglomeration and a lower rate of coke formation than the unpromoted Pt/KL. On all the catalysts, the amount of carbon deposits was greater in the presence of sulfur and after exposure to water vapor than under the reaction with clean feeds. This difference was explained in terms of metal particle growth and location in the zeolite.

Methods and Materials: The absorption spectra at the Pt L2 (13,273 eV) and L3 (11,564 eV) edges for fresh and spent Pt/KL and Pt/Ce-KL catalysts were measured at line X-18B, at the National Synchrotron Light Source (NSLS). The measurements were conducted in a stainless steel sample cell that allowed in-situ pretreatments at temperatures ranging from liquid nitrogen to 500oC. Prior to each measurement, the catalysts, previously reduced ex-situ at 500oC, were re-reduced in situ at 300oC (heating rate of 10oC(min)-1) for 30 min in flowing H2. After the reduction step, the sample was cooled down under flowing He. The X-ray absorption spectra were recorded at liquid nitrogen temperatures under He flow. Six scans were recorded for each sample. The average spectrum was obtained by adding the six scans. The pre-edge background was subtracted by using power series curves. Subsequently, the post-edge background was removed using a cubic-spline routine. The spectra were normalized to the height of the adsorption edge. The range in k-space used for the analysis was 3.0 - 15 Å⁻¹. To avoid overemphasizing the low energy region the c data were k³-weighted []. Absorption data obtained on a Pt foil at liquid nitrogen temperature was used as an experimental reference for the Pt-Pt bond (C.N. = 12, R = 0.275 nm).

Results: Figure 1 shows the Fourier transforms of the X-ray absorption data collected on the two samples. A slight difference was observed in the satellite peak to the left of the main Pt-Pt peak, but otherwise the spectra were almost identical, indicating that the Pt clusters in the two catalysts are very similar. In agreement with this qualitative observation, the quantification of the EXAFS data done using the BAN software indicates that the structural parameters of the Pt clusters are very similar in both catalysts in the freshly reduced state. The L3 and L2 absorption edges of Pt include intra-atomic transitions from the occupied 2p levels to unoccupied 5 d levels. As pointed out by Ramaker et al. there are significant differences among the transitions involved in each of the two edges. Specifically, as illustrated in Figure 2, the L3 edge includes transitions from the 2p_{3/2} level to the 5d_{5/2} and 5d_{3/2} levels, but the L2 edge only includes a transition from the 2p_{1/2} level to the 5d_{3/2}. The L3 and L2 absorption edges for Pt on the unpromoted and Ce-promoted Pt/KL (VPI) catalysts were compared to those of a Pt foil. As expected The L3 and L2 spectra of a given sample had the same EXAFS oscillations. Therefore, the edges could be aligned in such a way to exactly superimpose the EXAFS part. This is the most reliable way to make comparisons of different absorption edges. As observed for the L2 edge, the first peak after the edge (white line), which is responsible for intra-atomic transitions was much smaller on the Pt/KL sample than on the Pt/Ce-KL or on the Pt foil. The difference between the Pt/KL and the Pt foil was interpreted in terms of the band narrowing, just due to particle size effects. However, the difference between the unpromoted Pt/KL and the Ce-promoted catalyst could not be explained in those terms, since both catalysts had comparably small Pt clusters. It was also demonstrated that the difference between Pt/KL and Pt/Ce-KL, although small in comparison with the size of the absorption edge, was large in comparison with the almost perfect match observed in the rest of the spectra. The enhanced absorption in the first peak after the edge would indicate that the 2p_{1/2} → 5d_{3/2} transition occurs to a greater extent on the Ce-promoted catalyst than on the Pt/KL catalyst. This enhancement could be due to either an electron transfer from the Pt to the Ce-promoted zeolite, which would depopulate the 5d_{3/2} level, or a shift in the Fermi level, not associated with an electron transfer, but only due to a change in the Madelung

potential of the zeolite around the Pt particle. Similar changes have been proposed for Pt supported on La³⁺-containing zeolites.

Conclusions We have found that although under clean conditions the addition of Ce or Yb causes a decrease in activity, the stability of the catalysts is greatly enhanced by the presence of the rare earths. This enhanced stability is also observed after exposure to a water-containing feed. We have ascribed the improved stability to an inhibition in the agglomeration of Pt particles, which normally occurs on the unpromoted Pt/KL catalysts. This inhibition can be linked to metal-support interactions that are enhanced by the presence of rare earth oxides and are made evident by XANES analysis. In the presence of sulfur, the addition of Ce and to a lesser extent Yb, significantly inhibit the deactivation of the catalysts. In this case, not only the more effective anchoring of the Pt clusters, but also the ability of Ce and Yb to capture sulfur may be responsible for the enhanced sulfur tolerance.

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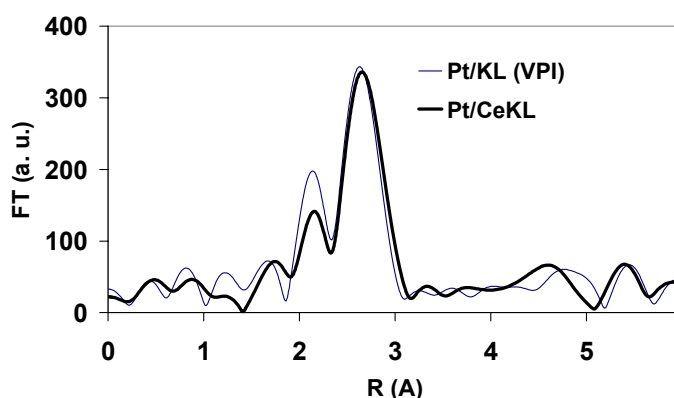


Figure 1. Fourier Transforms corresponding to the k₃-weighted Pt L₃-edge EXAFS spectra obtained at liquid nitrogen temperature on in-situ reduced Pt/KL and Pt/Ce-KL catalysts.

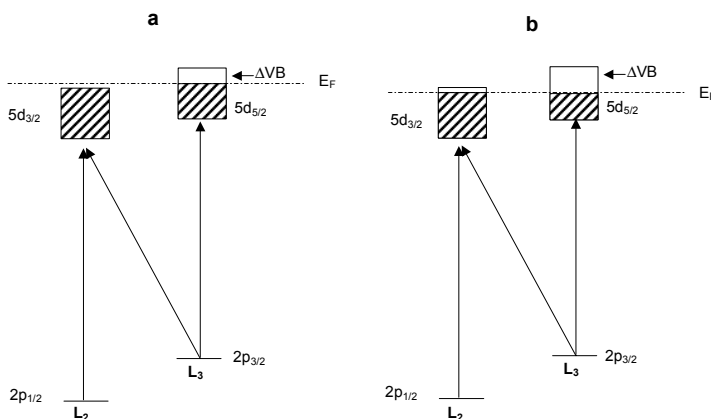


Figure 2. L₃ and L₂ edge scheme showing that the transitions are from the 2p_{3/2} level to the 5d_{5/2} and 5d_{3/2} in the case of L₃ and from the 2p_{1/2} level to the 5d_{3/2} for L₂.